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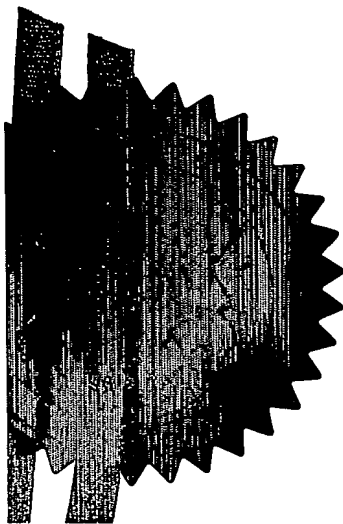
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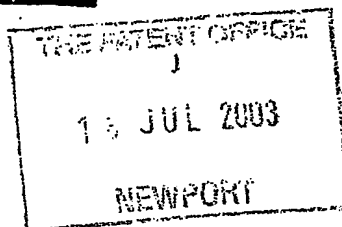
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18 JUL 2003

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1. Your reference

SMC 60605/GB/P1

2. Patent application number

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0316855.6

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number (if you know it)

07764137001 ✓

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

Inks, Compounds and Processes

5. Name of your agent (if you have one)

MORPETH, Fraser Forrest

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Avecia Limited  
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United Kingdom

Patents ADP number (if you know it)

07764137001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

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Date of filing  
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
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11.

I/We request the grant of a patent on the basis of this application.

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SMC 60605

APPLICANTS

AVECIA LIMITED

TITLE

INKS, COMPOUNDS AND PROCESSES

INKS, COMPOUNDS AND PROCESSES

This invention relates to inks, to compounds, to printing processes, to printed substrates and to ink-jet printer cartridges.

5 Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate. The set of inks used in this technique typically comprise yellow, magenta, cyan and black inks.

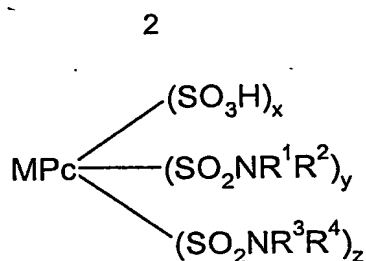
10 With the advent of high-resolution digital cameras and ink-jet printers it is becoming increasingly common to print off photographs using an ink-jet printer. This avoids the expense of conventional silver halide photography and provides a print quickly without the need to post a film to a developing service and wait days or weeks for it to be developed and returned.

15 While ink-jet printers have many advantages over other forms of printing and image development there are still technical challenges to be addressed. For example, there are the contradictory requirements of providing ink colorants which are soluble in the ink medium and yet do not run or smudge excessively when printed on paper. The inks need to dry quickly to avoid sheets sticking together after they have been printed, but they should not form a crust over the tiny nozzle used in the printer. Storage stability is also important to avoid particle formation that could block the tiny nozzles used in the printer.  
20 Furthermore, the resultant images desirably do not fade rapidly on exposure to light or common oxidising gases such as ozone.

Most cyan colorants used in ink-jet printing are based on phthalocyanines and problems of fading and shade change on contact with ozone are particularly acute with dyes of this class especially when they are printed onto media containing inorganic  
25 particles such as silica and/or alumina. There appears to be some aspect of the environment on the surface of such media (particularly media used for photo-realistic ink-jet printing) that promotes deterioration of these dyes in the presence of ozone.

WO99/67334 describes a new class of phthalocyanine that display considerable promise in ink-jet printing. One phthalocyanine in particular, which carries sulfo, sulfonamide and hydroxyethyl sulfonamide substituents, seems to have an optimum  
30 balance of the properties required in a dye for use in ink-jet printing. We have surprisingly found that when this favoured analogue bears substituents only in the  $\beta$  position of the phthalocyanine ring it yields prints with an enhanced ozone fastness.

Thus, the present invention provides a composition comprising:  
35 (a) a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is optionally substituted C<sub>1-4</sub>-hydroxyalkyl;

x is 0 to 3.9;

y is 0 to 3.9;

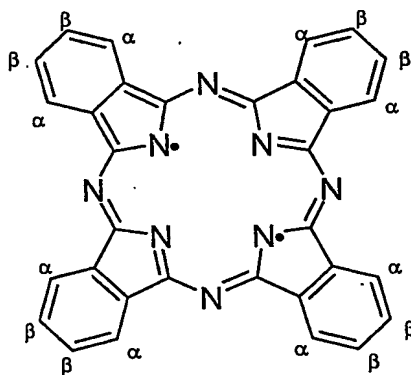
z is 0.1 to 4;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a β position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

The phthalocyanine nucleus may be represented by the bivalent radical of formula:



When a dye of Formula (1) is made by the more usual route of sulfonating a phthalocyanine pigment followed by chlorination and then amination/amidation then the resultant product carries sulfo and sulfonamide substituents in any susceptible position.

Details of the usual route for forming a compound of Formula (1) may be found in WO99/67334, Example 1, which is incorporated herein by reference.

The copper phthalocyanine dyes of Formula (1) where the substituents are attached to a β position on the phthalocyanine ring may be prepared by any method known in the art, and particularly by cyclisation of appropriate β substituted phthalic acid,

phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable copper or nickel salt, for example  $\text{CuCl}_2$ , followed by chlorination and then amination/amidation.

Preferably copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a  $\beta$  position on the phthalocyanine ring are prepared by cyclisation of 4-sulfo-phthalic acid to phthalocyanine  $\beta$  tetrasulfonic acid. The phthalocyanine  $\beta$  tetrasulfonic acid is then chlorinated and the sulfonyl chloride groups so formed are reacted with compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as hereinbefore defined. This reaction is preferably performed in water at a pH above 7. Typically the reaction is performed at a temperature of 30 to 70°C and is usually complete in less than 24 hours. The compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  may be used as a mixture or added sequentially.

Many of the compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  are commercially available, for example ammonia and ethanolamine, others may be made easily by a skilled person using methods which are well known in the art.

The ratio of sulfo to the two-sulfonamide substituents may be varied independently by varying the nature and amount of chlorinating agent used, the relative amounts of compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$  used and the reaction conditions in both reactions.

When phthalocyanine  $\beta$  tetrasulfonic acid is an intermediate in a route to compounds of Formula (1) it may be chlorinated by reacting with any suitable chlorinating agent.

Chlorination is preferably carried out by treating the phthalocyanine  $\beta$  tetrasulfonic acid with chlorosulfonic acid preferably in the presence of an acid halide such as thionyl chloride, sulfonyl chloride, phosphorous pentachloride, phosphorous oxychloride or phosphorous trichloride.

Preferably M is Cu.

Preferably  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or methyl, more preferably  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are all H.

$\text{R}^4$  may comprise more than 1 hydroxy group, although preferably  $\text{R}^4$  comprises a single hydroxy.

Preferably  $\text{R}^4$  is unsubstituted  $\text{C}_{1-4}$ -hydroxyalkyl, more preferably  $\text{C}_2$ -hydroxyalkyl.

Preferred optional substituents which may be present on  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently selected from: optionally substituted alkoxy (preferably  $\text{C}_{1-4}$ -alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene oxide or polypropylene oxide), carboxy, phosphato, sulfo, nitro, cyano, halo, ureido,  $-\text{SO}_2\text{F}$ , hydroxy, ester,  $-\text{NR}^5\text{R}^6$ ,  $-\text{COR}^5$ ,  $-\text{CONR}^5\text{R}^6$ ,  $-\text{NHCOR}^5$ , carboxyester, sulfone, and  $-\text{SO}_2\text{NR}^5\text{R}^6$ , wherein  $\text{R}^5$  and  $\text{R}^6$  are each independently H or optionally substituted alkyl

(especially C<sub>1-4</sub>-alkyl). Optional substituents for any of the substituents described for R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be selected from the same list of substituents.

It is especially preferred that R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are all H and R<sup>4</sup> is C<sub>1-4</sub>-hydroxyalkyl, particularly -CH<sub>2</sub>CH<sub>2</sub>OH.

5 Preferably x has a value greater than 0, more preferably x has a value of 0.1 to 3.8 and especially 0.5 to 3.5.

Preferably y has a value greater than 0, more preferably x has a value of 0.1 to 3.8 and especially 0.5 to 3.5.

In one preferred embodiment x and y are both 0 and z is 4.0.

10 The compounds of Formula (1) are also preferably free from fibre reactive groups. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of  
15 fibre reactive groups excluded from the compounds of Formula (1) there may be mentioned aliphatic sulfonyl groups which contain a sulfate ester group in beta-position to the sulfur atom, e.g. beta-sulfato-ethylsulfonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids, for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also  
20 the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of vinylsulfonyl- or beta-chloroethylsulfonyl- or beta-sulfatoethyl-sulfonyl-endo- methylene cyclohexane carboxylic acids. Other examples of  
25 cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl carbonyl; activated halogenated 1,3-dicyanobenzene radicals; and heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms in the heterocyclic ring and at least one cellulose reactive substituent on a carbon atom of the ring, for example a triazinyl halide .

30 Acid or basic groups on the compounds of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and in salt form.

Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as  
35 ((CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>) and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted into a salt using known techniques.

40 The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.



When the preferred route, as set out above, is used to synthesise compounds of Formula (1) then they are predominantly formed as ammonium salts. However, any known techniques may be used to exchange ammonia for another cation for example, acidification, optionally followed by dialysis, to remove the original cations with subsequent addition of alternative cations (e.g. by addition of alkali metal hydroxide, ammonium salt or amine). Use of ion exchange resins and reverse osmosis are other techniques for cation exchange.

When the medium (b) comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C<sub>1-8</sub>-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl ethers of diols, more preferably mono- C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50° to 125°C. The organic solvent

may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably  $\text{CH}_2\text{Cl}_2$ ; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent then preferably a polar solvent is preferably included since this enhances solubility of the compound of Formula (1) in the liquid medium. Examples of polar solvents include  $\text{C}_{1-4}$ -alcohols.

It is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a  $\text{C}_{1-4}$ -alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may of course contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I. Direct Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

It is preferred that the composition according to the invention is an ink suitable for use in an ink-jet printer. Ink suitable for use in an ink-jet printer is an ink which is able to repeatedly fire through an ink-jet printing head without causing blockage of the fine nozzles.

The inks may be incorporated in an ink-jet printer as a high concentration cyan ink, a low concentration cyan ink or both a high concentration and a low concentration ink. In the latter case this can lead to improvements in the resolution and quality of printed images. Thus the present invention also provides a composition where component (a) is present in an amount of 2.5 to 7 parts, more preferably 2.5 to 5 parts (a high concentration ink) or component (a) is present in an amount of 0.5 to 2.4 parts, more preferably 0.5 to 1.5 parts (a low concentration ink).

An ink suitable for use in an ink-jet printer preferably has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C.

An ink suitable for use in an ink-jet printer preferably contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a colorant of Formula (1) or any other component of the ink).

Preferably an ink suitable for use in an ink-jet printer has been filtered through a filter having a mean pore size below 10 $\mu$ m, more preferably below 3 $\mu$ m, especially below 2 $\mu$ m, more especially below 1 $\mu$ m. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

Preferably an ink suitable for use in an ink-jet printer contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

Preferred compositions comprise:

- (a) from 0.01 to 30 parts of compounds of Formula (1); and
- (b) from 70 to 99.99 parts of a liquid medium;

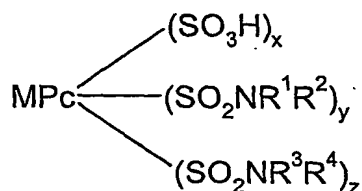
wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Compositions according to the present invention yield prints that display a good fastness to water and light. In particular, prints prepared using these inks display excellent light and ozone fastness.

A second aspect of the invention provides a compound of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

$R^1$ ,  $R^2$  and  $R^3$  independently are H or optionally substituted  $C_{1-4}$ alkyl;

$R^4$  is optionally substituted  $C_{1-4}$ -hydroxyalkyl;

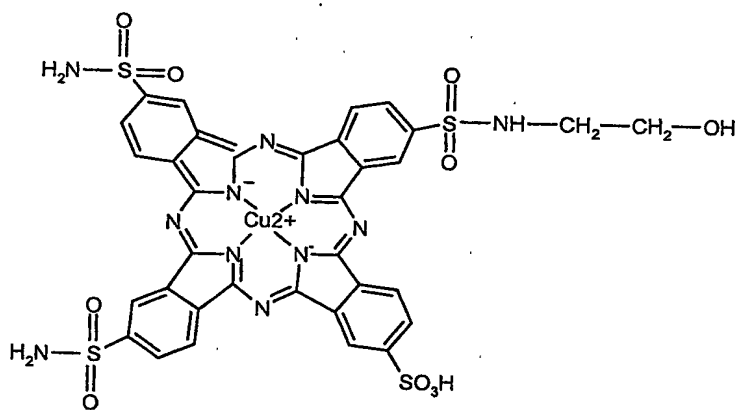
x is 0 to 3.9;

y is 0 to 3.9;

z is 0.1 to 4;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a  $\beta$  position on the phthalocyanine ring; and provided the compound of Formula (2) is not of formula



M,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , x, y and z are all as preferred in the first aspect of the invention.

It is especially preferred that  $R^1$ ,  $R^2$  and  $R^3$  are all H and  $R^4$  is  $-CH_2CH_2OH$ .

The compounds of Formula (2) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular they display excellent light and ozone fastness. Furthermore they may be prepared from cheap intermediates, avoiding the complexity and expense which is involved in manufacturing some of the more elaborate phthalocyanines.

A third aspect of the invention provides a composition which comprises a compound of Formula (2) as defined in the second aspect of the invention and water.

It is preferred that the composition according to the third aspect of the invention is an ink suitable for use in an ink-jet printer.

The ink according to the third aspect of the invention may contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the ink of the third aspect of the invention to modify the shade and performance properties. Examples of

such colorants include C.I. Direct Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

5 A fourth aspect of the invention provides a process for forming an image on a substrate comprising applying an ink according to the first or third aspect of the invention thereto by means of an ink-jet printer.

10 The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal  
15 causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO00/48938 and International Patent Application WO00/55089.

20 The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Glossy papers are especially preferred.

25 A fifth aspect of the present invention provides a material preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers printed with a composition according to the first or third aspects of the invention, a compound according to the second aspect or by means of a process according to the fourth aspect of the invention.

It is especially preferred that the printed material of the fifth aspect of the invention is a photograph printed by a process according to the fourth aspect of the invention.

30 A sixth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the first or third aspect of the present invention. The cartridge may contain a high concentration ink and a low concentration ink, as described in the first aspect of the invention, in different chambers.

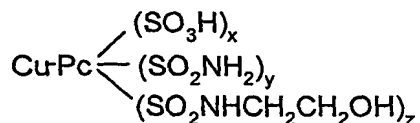
35 The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1Analysis of compounds of Formula (1)

Conformation of the structure of compounds of Formula (1) is by mass spec.

Elemental analysis is used to determine the ratios of x to y + z. Thus, when the sum of x plus y and z is not exactly 4 this is due to the presence of impurities. The presence of these impurities and their effect on the estimated values of x, y and z would be well known to a person skilled in the art who would appreciate that the value of x plus y plus z will not exceed 4 and who would treat the experimentally determined values of x, y and z as indicative of the true ratios of the groups.

Preparation of the following dye substituted only in the  $\beta$  position wherein x is 1.0, and (y + z) is 3.4:

Stage 1 - Preparation of copper phthalocyanine substituted with 4-SO<sub>3</sub>H groups in the  $\beta$  position

Potassium 4-sulfophthalic acid (56.8g), urea (120g), CuCl<sub>2</sub> (6.9g), ammonium molybdate (1.2g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.5g) were mixed in a reaction vessel. The mixture was then warmed in stages (130°C/30 minutes, 150°C/30 minutes, 180°C/30 minutes, 220°C) over 2 hours and the melt which formed was stirred at 220°C for a further 2 hours. The solid which formed was extracted 4 times with hot water (4 x 200ml) and the extract was filtered to remove insoluble material. The resultant filtrate was stirred at between 60°C – 70°C and then sufficient NaCl was added to give a 7% salt solution. Stirring was continued and the solid that precipitated was filtered, washed with a 10% salt solution (200 ml) and pulled dry by vacuum. The resultant damp solid (77.6g) was slurried in acetone, filtered and dried first at room temperature and then at 50°C.

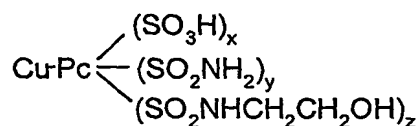
Stage 2 Preparation of the title product

Phosphorous oxychloride (2.43g) was added dropwise to chlorosulfonic acid (54.3g) over 5-10 minutes while keeping the temperature below 30°C. When all the POCl<sub>3</sub> had been added, the product of stage 1 (21g) was added portion-wise while keeping the reaction temperature below 60°C, this addition took 20-30 minutes. The reaction mixture was stirred at 50-60°C for 15-20 minutes. The temperature of the reaction mixture was then gradually increased to 138-140°C over 30 minutes and the reaction mixture was

stirred at this temperature for 3 hrs 30 minutes. The mixture was then allowed to cool to room temperature and stirred overnight. A further portion of  $\text{POCl}_3$  (1.2 ml) was added to the reaction mixture which was reheated to  $138^\circ\text{--}140^\circ\text{C}$  and stirred for a further 1 hour 30 minutes. The mixture was then cooled to room temperature and added to a mixture of water/ice/ $\text{NaCl}$ / concentrated  $\text{HCl}$  (100ml/200g/5g/3ml). The solid which precipitated was filtered, washed with ice cold acidified 5% salt solution and pulled dry using a vacuum pump. The resultant damp paste was added portion-wise to a mixture of ethanolamine/35% ammonia solution /water (1.25g/1.3ml/200ml) at  $0^\circ\text{--}10^\circ\text{C}$ . The mixture was adjusted to pH 8.5 and stirred at  $10^\circ$  to  $20^\circ\text{C}$  for 18 hours. The reaction mixture was then warmed to  $40 \pm 2^\circ\text{C}$  and the pH was adjusted to 12.8-13.0 with 2M  $\text{NaOH}$  and stirred for 5-6 hours. At the end of this time sufficient  $\text{NaCl}$  was added to the reaction mixture to give a 20% solution and the pH was adjusted to less than 1 with concentrated  $\text{HCl}$ . The solid which precipitated was filtered, washed with an acidified 10% salt solution ( $\text{pH} < 1$ ) and pulled dry using a vacuum pump. The resultant damp solid was dissolved in deionised water at pH 7, dialysed, filtered and then dried at  $50^\circ\text{C}$  to give 12.6g of product.

#### Example 2

Preparation of the following dye substituted only in the  $\beta$  position wherein x is 0.7 and (y + z) is 3.4:



The procedure of Example 1 was repeated except that in stage 2 the following amounts of reagents were used:

Copper phthalocyanine substituted with 4- $\text{SO}_3\text{H}$  groups in the  $\beta$  position  
from stage 1 – 11.8g

Chlorosulfonic acid - 69.9g

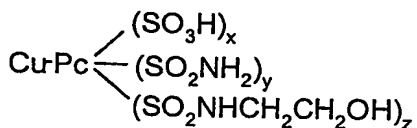
$\text{POCl}_3$  - 6.99g

Ethanolamine - 1.61g

Concentrated ammonia solution (35%) – 0.8g

#### Example 3

Preparation of the following dye substituted only in the  $\beta$  position wherein x is 0.3, y is 0 and z is 4.1:



The procedure of Example 1 was repeated except that in stage 2 the following amounts of reagents were used:

- 5 Copper phthalocyanine substituted with 4-SO<sub>3</sub>H groups in the β position  
from stage 1 –11.16g  
Chlorosulfonic acid - 116.5g  
PCl<sub>3</sub> (6.87g) was used in place of POCl<sub>3</sub>  
Ethanolamine – 6.7g.

#### 10 Inks

Inks of the present invention may be prepared by dissolving 3.5g of the dye of Examples 1 to 3 in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

#### 15 Further Inks

The inks described in Tables A and B may be prepared using the compounds made in Example 1 to 3. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

25 DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

30 P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na<sub>2</sub>HPO<sub>4</sub> and

TBT = tertiary butanol

35 TDG = thiodiglycol



TABLE A

Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2			5	1	
3	10.0	85	3	8	3	3						1
1	2.1	91						0.2	4		9	5
2	3.1	86	5				0.5	0.5	6	10	5	4
3	1.1	81			9	3			10			
1	2.5	60	4	15	3	3				6		5
2	5	65		20		5						
3	2.4	75	5	4		10		0.3	5	4	6	5
1	4.1	80	3	5	2	6				4		
2	3.2	65		5	4				5	4		
3	5.1	96										
1	10.8	90	5						5		4	
2	10.0	80	2	6	2	5			1		15	
3	1.8	80		5							5	
1	2.6	84			11							6
2	3.3	80	2			10				2		
3	12.0	90				7	0.3		3			3
1	5.4	69	2	20	2	1					3	
2	6.0	91			4						5	

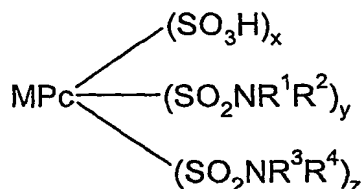
TABLE B

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
2	9.0	90		5						1.2		5
3	1.5	85	5	5		0.15	5.0	0.2				
1	2.5	90		6	4					0.12		6
2	3.1	82	4	8		0.3						
3	0.9	85		10					5	0.2		
1	8.0	90		5	5			0.3				
2	4.0	70		10	4				1			11
3	2.2	75	4	10	3				2			
1	10.0	91			6							
2	9.0	76		9	7		3.0			0.95		
3	5.0	78	5	11								
1	5.4	86			7							
2	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1		
3	2.0	90		10								
1	2	88										
2	5	78			5			10				
3	8	70	2		8			12			5	
1	10	80						15			5	
2	10	80		10				8			12	

CLAIMS

1. A composition comprising:

(a) a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is optionally substituted C<sub>1-4</sub>-hydroxyalkyl;

x is 0 to 3.9;

y is 0 to 3.9;

z is 0.1 to 4;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a β position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

2. A composition according to claim 1 wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or methyl.

3. A composition according to either claim 1 or claim 2 wherein R<sup>4</sup> is unsubstituted C<sub>1-4</sub>-hydroxyalkyl.

4. A composition according to any one of the preceding claims wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are all H and R<sup>4</sup> is -CH<sub>2</sub>CH<sub>2</sub>OH.

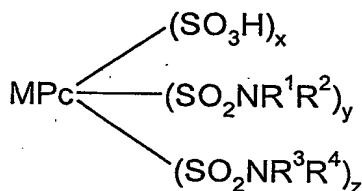
5. A composition according to any one of the preceding claims wherein M is Cu.

6. A composition according to any one of the preceding claims wherein x is 0.5 to 3.5.

7. A composition according to any one of the preceding claims wherein y is 0.5 to 3.5.

8. A composition according to any one of the preceding claims wherein x and y are both 0 and z is 4.0.

9. A compound of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

$\text{R}^4$  is optionally substituted  $\text{C}_{1-4}$ -hydroxyalkyl;

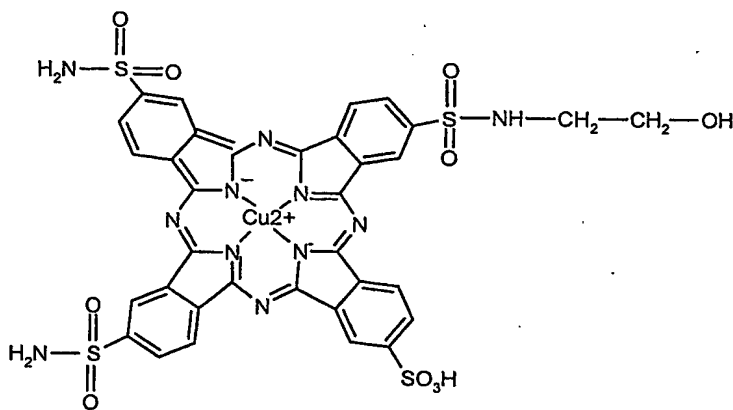
x is 0 to 3.9;

y is 0 to 3.9;

z is 0.1 to 4;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a  $\beta$  position on the phthalocyanine ring; and provided the compound of Formula (2) is not of formula



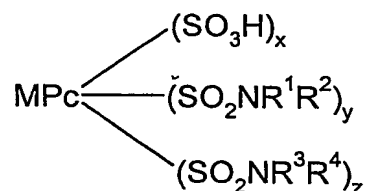
10. A compound according to claim 9 wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are all H and  $\text{R}^4$  is  $-\text{CH}_2\text{CH}_2\text{OH}$ .

11. A composition which comprises a compound of Formula (2) as defined in either claims 9 or 10 and water.
- 5 12. A process for forming an image on a substrate comprising applying a composition according to any one of claims 1 to 8 or 11 thereto by means of an ink-jet printer.
13. A material printed with a composition according to any one of claims 1 to 8 or 11 or a compound according to either claims 9 or 10.
- 10 14. A material according to claim 13 which is a photograph printed using a process according to claim 12.
- 15 15. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in any one of claims 1 to 8 or 11.

ABSTRACT  
INKS, COMPOUNDS AND PROCESSES

A composition comprising:

- 5 (a) a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

10 wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are H or optionally substituted C<sub>1-4</sub>alkyl;

R<sup>4</sup> is optionally substituted C<sub>1-4</sub>-hydroxyalkyl;

15 x is 0 to 3.9;

y is 0 to 3.9;

z is 0.1 to 4;

the sum of (x+y+z) is 4; and

20 the substituents, represented by x, y and z, are attached to a β position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water. Also novel compounds, ink-jet printing processes, printed images, printers and cartridges.

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